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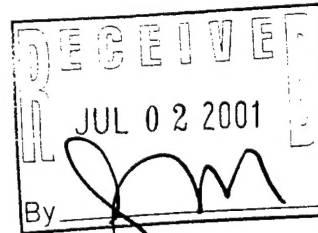
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Final Report

A NOVEL SYNTHESIS TECHNIQUE FOR SEMICONDUCTOR THIN FILM AND HETEROSTRUCTURE FORMATION

Grant number #DAAG55-98-1-0449

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(J.E. Rowe, Program Officer)

FORWARD:

The underlying concept in this proposal is to understand and employ the process of hydrogen induced cleaving for the manipulation of materials, and the formation of new group IV heterostructures. The major tasks in the proposal were:

1. Atomic level investigations of the implanted hydrogen/semiconductor interaction to provide a detailed description of the dynamics and defect interactions of hydrogen complexes;
2. Application of the hydrogen cleaving process to new materials, primarily SiC.

STATEMENT OF THE PROBLEM AND IMPORTANT RESULTS:

1. Atomic level investigations

We have carried out a number of key experiments to describe the dynamics and defect interactions of implanted hydrogen into silicon. **This experiment reports the first measurement of the vibrational state lifetime of a local mode impurity in a crystalline semiconductor.** The measured lifetime is 8.0 ± 0.2 psec, much shorter than the lifetimes of comparable H-Si (surface) systems. The qualitative understanding of this short lifetime depends on the interaction of the excited mode with the phonons of the system. Not only does this experiment reveal new fundamental information concerning the dynamics of vibrational mode excited states, but it also allows us to evaluate the feasibility of multiple excitation processes via tuned IR sources.

Hydrogen is an important impurity in semiconductors because of its ability to react with lattice imperfections, which often leads to removal of unwanted electronic states from the band gap. For instance, hydrogen passivation of defects is used routinely in the fabrication of Metal-On-Semiconductor (MOS) transistors, a key element in many integrated circuits, where hydrogen removes detrimental electronic states at the Si/SiO₂ interface. Lyding *et al* recently reported that passivation of MOS structures by deuterium instead of hydrogen increases the lifetime of such devices by 10 – 50 times [1]. Several mechanisms have been proposed to explain this giant isotope effect, including excitation

to anti-bonding electronic states [1] and excited vibrational states by hot electrons [1,2]. However, the physical parameters (scattering cross sections, vibrational lifetimes etc.) governing these mechanisms are essentially unknown, which has prohibited identification of the dominating degradation mechanism. This work provides new insight into the time-scales for dissipation of energy from excited vibrational states of Si-H and Si-D bonds and, thus, delineates the role of excited vibrational states in the degradation process.

A case study of the vibrational dynamics of Si-H and Si-D bonds was performed by focusing on the stretching mode of hydrogen at the bond-center site (H_{BC}) in crystalline silicon. The mode corresponding to vibration of the H atom along the Si-H-Si axis gives rise to an absorption line at 1998 cm^{-1} , and is particularly well suited for the experiments reported here because it has an unusually large absorption cross section. If hydrogen is substituted with deuterium (forming D_{BC}), the absorption line shifts down in frequency to 1449 cm^{-1} . H_{BC} (or D_{BC}) was produced by implanting protons (deuterons) into silicon single crystals. To combine a high area density of H_{BC} (D_{BC}) with a low volume concentration, protons (deuterons) were implanted at multiple energies with the dose at each energy adjusted to yield a uniform concentration profile. H_{BC} and D_{BC} are unstable at room temperature, and in order to prevent them from diffusing, the implantations were performed below 80 K, and the samples were kept at cryogenic temperatures until the spectroscopic measurements had been performed.

The lifetime of the 1998-cm^{-1} mode of H_{BC} was measured with the transient bleaching technique. In short, this technique uses light from a pulsed, infrared laser tuned into resonance with the 1998-cm^{-1} line to excite a significant fraction of the H_{BC} centers from the vibrational ground state to the first-excited state of the 1998-cm^{-1} mode. The excitation leads to a partial bleaching of the fundamental transition of the mode, which is observed as a transient increase, ΔT , in the transmission coefficient of the sample at 1998 cm^{-1} . The decay of ΔT after excitation is given by the decay of H_{BC} defects from the first-excited state to the ground state. The decay is exponential with a time constant (lifetime) $T_1 = 7.8 \pm 0.2\text{ ps}$. This is the first measurement of the lifetime of a local vibrational mode in a semiconductor, and shows that Si-H bonds in the bulk relax much faster upon excitation than Si-H bonds on surfaces, where lifetimes of the order of nanoseconds are observed [4].

The experiments presented here have provided important new insight into the vibrational relaxation of Si-H and Si-D bonds. In particular, it has shown that relaxation times are two orders of magnitude shorter in the bulk than at surfaces. Moreover, no major difference was found between the lifetimes of Si-H and Si-D stretch modes, which indicates that such modes are unlikely to be responsible for the difference in degradation of hydrogenated and deuterated MOS structures.

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2. Hydrogen induced cleaving of SiC

One underlying motivation for this work is to evaluate the feasibility of forming SiC heterostructures via "thin film slicing" of a single SiC substrate. SiC is an important materials for high power, high temperature devices, critical to defense needs. Nevertheless the high cost of SiC is a major obstacle to the realization of this goal. A successful bonding process will allow multiple uses of a single substrate and thus reduce costs. We have carried out extensive investigations of the hydrogen implantaion induced cleaving process in SiC. The work has focused on the formation and exfoliation of gas induced blisters, a necessary precursor for bonding. In general, the larger the blister created, the more efficient the bonding. Our investigations have lead to two important discoveries: 1) There is a sharp maximum in mature blister size as a function of dose. This comes about as a result of a trade-off between ion induced defects and critical hydrogen concentration and 2) a new process for complete exfoliation, involving a second, heavy-ion implant which causes a stress induced complete exfoliation of the hydrogen implanted area. **This is the first time "complete exfoliation" has been reported in SiC.** Such complete exfoliation assures a successful bonding and provides a new method of micromachining SiC.

The process of hydrogen induced cleaving in silicon has been very successful and given rise to the new interest in silicon-on-insulator structures. The cleaving process in silicon is a delicate balance between internal cavity formation, due to defect agglomeration and internal hydrogen passivation of the cavities. SiC a much stiffer material has, up to now, resisted this simple cleaving process. In our modified process we exploit the fact that implanted SiC forms an amorphous layer with a substantially different density than the crystalline form. (This is not the case in silicon, where amorphous and crystalline density are within a few % of one another.) The large density difference induces a stress which is terminated at the implanted hydrogen layer, probably with the onset of dislocations. At elevated temperature surface energy considerations drive the interface structure to instability and relaxation via the cleavage process.

Subsequent to our discovery of the double implant process, it was recognized that surface smoothing of the cleaved surface will be a critical component of the "cleave and bond process". Through scientific contacts and with the support of ARO/ARL we established a new facet of our program with Dr. James Hirvonen (ARL/Md), an expert in a new surface smoothing process involving lateral sputtering via energetic cluster beams. Using analytical tools at Vanderbilt we measured the surface smoothing and lattice damage of SiC samples irradiated at Epion Corporation with Hirvonen and collaborators. It was established that the ion beam smoothing process is very applicable to the SiC smoothing process, showing reductions in RMS roughness of one order of magnitude, under optimum bombardment conditions. These conditions were established through the ARL/Vanderbilt/Epion cooperation.

Papers Published:

1) Peer reviewed journals:

Vacancy-hydrogen Complexes in Group IV-Semiconductors, M. Budde, B. Bech Nielsen, J.C. Keay and L.C. Feldman, Physics B **273**, 208 (1999).

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2) Conference proceedings:

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Invited talk, APS Meeting , 2001

Polishing of Silicon Carbide with Gas Cluster Ion Beams, V. DiFilippo, J. Bennett, D. Fenner, L.C. Feldman, A. Saigal, APS March Meeting, 2001.

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Dr. W. Holland (ORNL) collaborator

Dr. J. K. Hirvonen (ARL)-collaborator

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